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Note on the Application of Near-Frozen Flow Criteria for One-Dimensional Nonviscous Expansion through a Laval Nozzle

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A GENERAL criterion for near-frozen adiabatic expansion in one-dimensional nonviscous flow through a Laval nozzle has been described in a recent publication.[1] Unfortunately it appears that the discussion was so condensed that it is hardly possible to apply the result, Eq. (28a), without a few explanatory remarks.

Near-frozen flow should be defined properly by Eq. (27) in terms of equilibrium constants based on mole fractions. However, in the special case $\Sigma_j(\nu_j''-\nu_j')=0$, which is of interest for most practical applications, the near-frozen flow criterion given in Eq. (28a) becomes identical with the criterion derivable from Eq. (27) with equilibrium constants expressed in terms of mole fractions.

In deriving Eq. (28a) from Eq. (28) it is obvious that the quantity $(d\ln K_e/dT)_{T'\cong T_c}$, which appears on the left-hand side of Eq. (28a), represents $(d\ln K_e/dT)_{T_c}(T_c-T')/(T_c-T)$. The quantity $d\ln K_e/dT$ appearing on the right-hand side of Eq. (28a) should have the single subscript T_c as in Eq. (28). For the important special case $\Sigma_j(\nu_j''-\nu_j')=0$, $(d\ln K_e/dT)_{T_c}=\Delta H/RT_c^2$ where ΔH equals the heat of reaction. It is then a simple matter to obtain an explicit relation for T_c-T'. The result, for $\Sigma_j(\nu_j''-\nu_j')=0$, is

$$T_c-T'=(RT_c^2/\Delta H)[K_e(T_c)/K_e(T)-1]\times\left\{1+[(-DT/Dt)K_e(T_c)/K_e(T)(T_c-T)]\times\left[k_f\Pi_j C_j^{\nu_j'}\Sigma_j\frac{(\nu_j''-\nu_j')^2}{C_j}\right]^{-1}\right\}^{-1} \quad (28b)$$

or, in most cases which are of practical interest,

$$(T_c-T')/(T_c-T)\leqslant(-DT/Dt)^{-1}(RT_c^2/\Delta H)k_f\times\Pi_j C_j^{\nu_j'}\Sigma_j\frac{(\nu_j''-\nu_j')^2}{C_j}. \quad (28c)$$

Thus the reduced temperature lag $(T_c-T')/(T_c-T)$ is proportional to the reaction rate and inversely proportional to the rate of change of temperature with time. For sufficiently large values of $(-DT/Dt)$ the chemical changes occurring during flow are always negligibly small.

For individual chemical reaction steps for which $\Sigma_j(\nu_j''-\nu_j')\neq 0$, near-frozen flow is best defined by the relation

$$K_x(T')\simeq K_x(T_c)-K_x(T_c)(d\ln K_x/dT)_{T_c}(T_c-T'), \quad (27a)$$

where $K_x=K_e(\Sigma_j C_j)^{\Sigma_j(\nu_j''-\nu_j')}$ is the equilibrium constant expressed in terms of mole fractions. From Eqs. (21) and (27a) it is then readily shown that

$$(d\ln K_x/dT)_{T'\simeq T_c}(-DT/Dt)=k_f\Pi_j C_j^{\nu_j'}[\Sigma_K(\nu_K''-\nu_K')^2/C_K]\times\{1-[K_e(T)/K_e(T_c)][\Sigma_j C_j(T')/\Sigma_j C_j(T_c)]^{\Sigma_j(\nu_j''-\nu_j')}\times[1+(d\ln K_x/dT)_{T_c}(T_c-T')]\}. \quad (29a)$$

Equation (28b) is now replaced by the relation

$$[\Delta H/RT_c^2+\Sigma_j(\nu_j''-\nu_j')\gamma/T_c(\gamma-1)]\times(T_c-T')(-DT/Dt)/(T_c-T)=k_f\Pi_j C_j^{\nu_j'}[\Sigma_K(\nu_K''-\nu_K')^2/C_K]\times\{1-[K_e(T)/K_e(T_c)](T'/T_c)^{\Sigma_j(\nu_j''-\nu_j')/(\gamma-1)}\times[1+(\Delta H/RT_c^2)(T_c-T')+\Sigma_j(\nu_j''-\nu_j')\gamma(T_c-T')/T_c(\gamma-1)]\}. \quad (29b)$$

From Eq. (29b) the following conservative near-frozen flow criterion is obtained for $d\ln K_x/dT>0$:

$$(T_c-T')/(T_c-T)\leqslant(-DT/Dt)^{-1}\times[\Delta H/RT_c^2+\Sigma_j(\nu_j''-\nu_j')\gamma/T(\gamma-1)]^{-1}\times k_f\Pi_j C_j^{\nu_j'}[\Sigma_K(\nu_K''-\nu_K')^2/C_K]. \quad (29c)$$

Representative applications of the preceding relations to separate chemical reaction steps can be worked out without difficulty and will be described elsewhere.

[1] S. S. Penner, J. Chem. Phys. 19, 877 (1951).